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Theory for thermodynamic and transport properties of molecular fluids

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Abstract · Using the 'preaveraged' pair potential method, we derive an effective Lennard-Jones (ELJ) (12-6) potential, which includes the influence of the angle-dependent part of potentials through the expressions of the effective diameter σ_f and well depth ε_f We employ this theory to calculate the thermodynamic properties, critical point location, surface tension and thermodynamic behaviour along the liquid-vapour coexistence curve of N_2 and O_2 The theory is further applied to calculate the transport properties such as the shear viscosity and thermal conductivity of N_2 . In all these cases, the agreement with the experimental data is good

Keywords Molecular fluids, thermodynamic properties, transport properties

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1. Introduction

Aim of the present paper is to compute the thermodynamic and transport properties of molecular fluids. A theoretical approach developed to deal with the thermodynamic properties of the molecular fluid is the perturbation theory in which either a spherically symmetric potential or non-spherical potential is taken as a reference potential and effect of electrostatic interactions is considered as a perturbation [1]. The spherically symmetric reference potential is suitable for weakly anisotropic pair potential. On the other hand, for strongly anisotropic pair potential, the non-spherical reference potential gives good convergence. In many molecular fluids such as nitrogen-like fluids, the repulsive core is slightly non-spherical. For such molecular fluids, a perturbation theory is employed in which the central potential is taken as a reference potential and the angle-dependent part of interaction as a perturbation [1-6]. The perturbation series for free energy is summed up using the Padc' approximant given by Stell *et al* [7].

Another method for calculating the thermodynamic properties of molecular fluids is the

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'preaveraged' potential method [7-9]. This method can be employed to estimate the thermodynamic properties of molecular fluids of weakly anisotropic potential.

Transport properties (TP's) of molecular fluid have aroused considerable interest in recent years [10, 11]. However, this is confined to the Gaussian overlap (G.O.) model [12]. No attempt has been made to calculate the TP's of molecular fluid, whose molecules interact *via* a pair interaction potential of the form

$$u(r, \omega_1, \omega_2) = u_0(r) + u_a(r, \omega_1, \omega_2), \tag{1}$$

where $u_0(r)$ is a spherically symmetric potential and $u_a(r, \omega_1, \omega_2)$ is the angle-dependent part of pair interaction. Here $r = | r_1 - r_2 |$ is the centre-to-centre distance and ω_i represents the orientational coordinates (θ_i, ϕ_i) of molecule i.

In the present work, we employ the 'preaveraged' potential method [9] to derive the effective pair potential, which includes the influence of the angle-dependent pair potential and may be a function of temperature T. This effective pair potential is used to calculate the thermodynamic and transport properties of molecular fluids.

In Section 2, we discuss the theoretical basis for obtaining the 'preaveraged' pair potential for a molecular fluid. This 'preaveraged' potential is expressed in the effective Lennard Jones (12-6) form. Section 3 is concerned with the evaluation of the thermodynamic properties. The critical point location, surface tension and liquid vapour coexistence curve are discussed in Sections 4, 5 and 6, respectively. Section 7 is devoted to calculate the transport properties of the system. The concluding remarks are given in Section 8.

2. Theoretical basis

We consider a molecular fluid of rigid linear molecules interacting *via* pair potential given by eq. (1), where $u_0(r)$ is the central potential and u_a is the angle dependent potential. For the central potential, we take the Lennard-Jones (LJ) (12-6) potential

$$u_0(r) = 4\varepsilon\left[(\sigma / r)^{12} - (\sigma / r)^6\right], \tag{2}$$

where ε and σ are, respectively, the well depth and molecular diameter. For angle dependent part, we take

$$u_a = u_{perm} + u_{in} + u_{dis} \tag{3}$$

where u_{perm} is the interaction between the parmanent multipole moments of the molecules, u_{in} is the interaction of the induced multipole moments in one molecule with the permanent multipole moments in other molecule and u_{dis} is the anisotropic dispersion potential. These interaction potentials can be expressed as an expansion in spherical harmonic [1]. For numerical calculation, however, we take the explicit angle-dependent form of interaction [1, 13].

The configuration integral Z_N is defined in this case as [1]

$$Z_N = \Omega^{-N} \int \ldots \int \exp\left[-\beta \sum_{i<j} u(x_i, x_j)\right] \prod_{i=1}^{N} dx_i, \tag{4}$$

where the vector $x_i \equiv (r_i \omega_i)$ represents both the position of the centre of mass and orientation of molecules i, $dx_i = dr_i\, d\omega_i$, $\Omega = 4\pi$ for linear molecule and $\beta = (kT)^{-1}$. Using eq. (1) in

eq. (4), we follow the method of Shukla *et al* [9] and express the configurational integral in the form

$$Z_N = \int \ldots \int \exp\left[-\beta \sum_{i<j} \Psi(r_{ij})\right] \prod_{i=1}^{N} dr_i , \tag{5}$$

where $\Psi(r_{ij})$ is the orientation-independent 'preaveraged' pair potential expressed as

$$\Psi(r) = u_{LJ}(r) + V(r), \tag{6}$$

where u_{LJ} is the *LJ* (12-6) potential and

$$V(r) = V_1(in) + V_2(perm) + V_2(anis\text{-}dis) + V_2(dis\text{-}in) + V_2(perm\text{-}dis) + V_3(perm) + V_4(perm). \tag{7}$$

The explicit expressions of these terms are reported elsewhere [9]. Using these expressions, eq. (6) can be expressed in a compact form

$$\Psi(r) = 4\varepsilon \left(A_{12}(\sigma / r)^{12} - \left[A_6(\sigma / r)^6 + A_8(\sigma / r)^8 + A_{10}(\sigma / r)^{10}\right]\right) + 4\varepsilon \left(A_{11}(\sigma / r)^{11} + A_{13}(\sigma / r)^{13} + A_{15}(\sigma / r)^{15}\right). \tag{8}$$

The explicit expressions of the coefficients A_m are given in Appendix A in terms of the following reduced quantities

$$T^* = kT / \varepsilon ,$$

$$\mu^{*2} = \mu^2 / \varepsilon\sigma^3 ,$$

$$Q^{*2} = Q^2 / \varepsilon\sigma^5 ,$$

$$\alpha^* = \alpha / \sigma^3 .$$

In the present calculation, we neglect the terms appearing in the second bracket of the right hand side of eq. (8), as their contributions are found to be relatively very small. For example, these coefficients at $T^* = 1.0$ are reported as for N_2

$$A_{11} = -9.775 \times 10^{-3},\ A_{13} = 0,\ A_{15} = -7.731 \times 10^{-4},$$

and for O_2

$$A_{11} = -1.787 \times 10^{-3},\ A_{13} = 0,\ A_{15} = -0.753 \times 10^{-6}.$$

This shows that their contribution to the effective potential may be neglected. Thus, we obtain an expression for the effective 'preaveraged' pair potential as

$$\Psi(r) = 4 \in \left(A_{12}(\sigma / r)^{12} - \left[A_6(\sigma / r)^6 + A_8(\sigma / r)^8 + A_{10}(\sigma / r)^{10}\right]\right). \tag{9}$$

The coefficients A_m given in the Appendix A, may be expressed in the forms

$$A_6 = 1 + (1/3)a^{*2} / T^* + d^* , \tag{10a}$$

$$A_8 = b^{*2}/T^* + (3/2)e^*, \tag{10b}$$

$$A_{10} = (7/5)c^{*2}/T^*, \tag{10c}$$

$$A_{12} = 1+(14/225)a^{*4}/T^{*3} - (4/5T^*)K^2(1+1.9K^2). \tag{10d}$$

They are expressed in terms of reduced quantities

$$a^* = \mu^2/2\varepsilon\sigma^3 = \mu^{*2}/2,$$

$$b^* = \mu Q/2\varepsilon\sigma^4 = \mu^* Q^*/2,$$

$$c^* = Q^2/2\varepsilon\sigma^5 = Q^{*2}/2,$$

$$d^* = \alpha\mu^2/2\varepsilon\sigma^6 = \alpha^*\mu^{*2}/2,$$

$$e^* = \alpha Q^2/2\varepsilon\sigma^8 = \alpha^* Q^{*2}/2. \tag{11}$$

Here, μ is the dipole moment, Q the quadrupole moment, α the polarizability and K is the anisotropy in the polarizability of the molecule.

The 'preaveraged' pair potential given by eq. (9) can be expressed in the form of the LJ (12-6) potential (eq. 2) by simply replacing

$$\sigma \rightarrow \sigma_T(T^*)$$

and

$$\varepsilon \rightarrow \varepsilon_T(T^*).$$

Thus, the angle-dependent part of potential modifies the values of σ and ε. In order to obtain expressions for σ_T and ε_T, we approximate $\sigma/r \approx \sigma/r_m = 2^{-1/6}$ [14] and write eq. (9) as

$$\Psi(r) = 4\varepsilon\left((\sigma/r)^{12}A_{12} - (\sigma/r)^6\left[A_6 + A_8 2^{-1/3} + A_{10}2^{-2/3}\right]\right). \tag{12}$$

Eq. (12) can be expressed in the LJ (12-6) form

$$\Psi(r) = 4\varepsilon_T\left[(\sigma_T/r)^{12} - (\sigma_T/r)^6\right], \tag{13}$$

where

$$\sigma^{\Lambda} \equiv \sigma_T/\sigma = F^{-1/6}, \tag{14a}$$

$$\varepsilon^{\Lambda} \equiv \varepsilon_T/\varepsilon = A_{12}F^2 \tag{14b}$$

and

$$F = \left[A_6 + A_8 2^{-1/3} + A_{10}2^{-2/3}\right]/A_{12}. \tag{15}$$

Thus, the effective pair potential can be expressed as the 'modified' LJ (12-6) form in terms of σ_T and ε_T. Then the molecular fluid can be treated as the LJ (12-6) system.

3. Thermodynamic properties of molecular fluids

We apply our theory to calculate the thermodynamic properties of molecular fluids. In our approach, we consider the reduced density $\rho^* = \rho\,\sigma^3$ and reduced temperature $T^* = kT/\varepsilon$ for the LJ (12-6) fluid and replace ρ^* by $\rho_T^* = \rho^*\sigma^{*3}$ and T^* by $T_T^* = T^*/\varepsilon^*$. Then the free energy and pressure of molecular fluid can be given by

$$A(\rho^*, T^*) = A_{LJ}(\rho_T^*, T_T^*), \tag{16}$$

$$P(\rho^*, T^*) = P_{LJ}(\rho_T^*, T_T^*), \tag{17}$$

where $A_{LJ}(\rho_T^*, T_T^*)$ and $P_{LJ}(\rho_T^*, T_T^*)$ are, respectively, the free energy and pressure of the LJ(12-6) fluid at the reduced density ρ_T^* and reduced temperature T_T^*.

3.1 Virial equation of state for dipole molecular fluid :

We may express the pressure of the molecular fluid in the virial form

$$\beta P/\rho = 1 + \sum_{n=2}^{\infty} B_n(T^*)/V^{n-1}, \tag{18}$$

where B_n is the nth virial coefficient which is given by

$$B_n(T^*) = (2\pi N\sigma^3/3)^{n-1} B_n^*(T^*) \tag{19}$$

with

$$B_n^*(T^*) = \sigma^{*3(n-1)} B_{nLJ}^*(T_T^*), \tag{20}$$

where $B_{nLJ}^*(T_T^*)$ is the reduced nth virial coefficient of the LJ(12-6) fluid at the reduced temperature T_T^*, which can be evaluated numerically and is available [15].

For example, we calculate the reduced second virial coefficient $B_2^*(T^*)$ for the dipolar LJ(12-6) fluid as a function of $t = \mu^{*2}/\sqrt{3}$ for different values of T^*. They are compared with the exact results [15] in Table 1. The agreement is found to be good for low value of μ^{*2} ($t \le 1.0$). The deviation increases with decrease of T^* and / or increase of t.

Table 1. The reduced second virial coefficient B_2^* for dipolar LJ(12-6) fluid as a function of $t = \mu^{*2}/\sqrt{8}$

T*	t = 0.1		t = 0.3		t = 0.5		t = 1.0	
	Present	Exact	Present	Exact	Present	Exact	Present	Exact
0.75	- 4.2971	- 4.2871	- 5.2407	- 5.2364	- 7.4836	- 7.5043	- 28.8490	- 30.4
1.00	- 2.5919	- 2.5889	- 3.0130	- 3.0102	- 3.9348	- 3.9406	- 9.3310	-10.54
1.50	- 1.2204	- 1.2197	- 1.3736	- 1.3728	- 1.6940	- 1.6931	- 3.4332	- 3.4903
2.00	- 0.6377	- 0.6375	- 0.7172	- 0.7169	- 0.8800	- 0.8799	- 1.7173	- 1.7265
2.50	- 0.3190	- 0.3187	-0.3679	- 0.3658	- 0.4670	- 0.4670	- 1.9839	- 0.9858
3.00	- 0.1195	- 0.1194	- 0.1529	- 0.1527	- 0.2201	- 0.2201	- 0.5516	- 0.5517

3.2 Thermodynamics for dense molecular fluid

This approach can be used to calculate the thermodynamic properties of dense molecular fluids. These properties can be calculated using the Verlet-Weis [16] version of the Weeks-Chandler-Andersen (WCA) [17] perturbation theory. However, we are interested here to calculate the thermodynamic properties such as Gibb's free energy G, enthalpy H and molar volume V at zero pressure using expressions due to Grundke *et al* [18].

We use this theory to calculate the thermodynamic properties of fluids N_2, O_2 and Ar at zero pressure. The force parameters of these systems are given in Table 2. The values of σ and ε for N_2 are used by Stephan *et al* [19]. The other force parameters are those used by Singh and Sinha [20]. The calculated values of G, H and V are compared with the molecular dynamic (MD) values [21] in Table 3 for N_2, O_2 and Ar at $P = 0$ and $T = 83.82$°K. The agreement is found to be good.

Table 2. Force parameters used in present calculation.

System	σ (°A)	ε / k (K)	$\alpha \times 10^{24}$ (Cm^3)	$Q \times 10^{26}$ (esu Cm^2)	K
N_2	3.650	100.017	1.730	− 1.40	0.176
O_2	3.388	122.440	1.600	− 0.39	0.239
Ar	3.405	199.800			

Table 3. Gibb's free energy G, enthalpy H and volume V for fluids at P = 0 and T = 83.82 K

System		− G/ (J mol^{-1})	− H (J mol^{-1})	V (Cm^3 $-mol^{-1}$)
N_2	Theory	2872.50	4844.89	35.91
	MD		4908.00	36.12
O_2	Theory	3994.25	6467.29	25.10
	MD		6443.00	27.24
Ar	Theory	3560.40	5852.72	28.41
	MD		6066.00	28.21

4. Critical point location

In this section, we employ our theory to study the critical temperature T_c, critical volume V_C and critical pressure P_C for molecular fluids. For the LJ (12-6) fluid they are given by

$$T_C^* \equiv kT_C / \varepsilon = 1.26, \tag{21a}$$

$$V_C^* \equiv V_C / N\sigma^3 = 3.1, \tag{21b}$$

$$P_C^* \equiv P_C\sigma^3 / \varepsilon = 0.117. \tag{21c}$$

In order to estimate the critical constants of molecular fluids, we replace $\varepsilon \rightarrow \varepsilon_T$ and $\sigma \rightarrow \sigma_T$ in eq. (21). Thus,

$$T_C^* = 1.26\,\hat{\varepsilon}, \tag{22a}$$

$$V_C^* = 3.1\,\hat{\sigma}^3, \tag{22b}$$

$$P_C^* = 0.117\hat{\varepsilon}/\hat{\sigma}^3. \tag{22c}$$

Eq. (22a) may be solved by the interative process. Knowing T_C*, one may obtain V_C* and P_C* .

We first consider the dipolar LJ(12-6) fluid. Using the expressions of $\hat{\varepsilon}$ and $\hat{\sigma}$ in eq. (22), we obtain

$$T_c^* = 1.26\left[1+(\mu^{*2}/2)^2/3T_c^*\right]^2/\left[1+(14/225)(\mu^{*2}/2)^4/T_c^{*3}\right], \tag{23a}$$

$$V_c^* = 3.1\left(\left[1+(\mu^{*2}/2)^2/3T_c^*\right]/\left[1+(14/225)(\mu^{*2}/2)^4/T_c^{*3}\right]\right)^{-1/2}, \tag{23b}$$

$$P_c^* = 0.117/\sqrt{1.26}\left[T_c^* 1+(\mu^{*2}/2)^2/3T_c^*\right]^{1/2}. \tag{23c}$$

Eq. (23a) can be rearranged and written as

$$T_c^* = 1.26\left[1+(2/3)(\mu^{*2}/2)^2(1/T_c^*)+0.061728(\mu^{*2}/2)(1/T_c^{*2})+\ldots\right]. \tag{24}$$

Using the interative process, it can be solved to give

$$T_c^* = 1.26+(2/3)(\mu^{*2}/2)^2-0.303743(\mu^{*2}/2)^4+\ldots. \tag{25}$$

From eq. (23a), we get

$$\left[1+(\mu^{*2}/2)^2/3T_c^*\right]/\left[1+(14/225)(\mu^{*2}/2)^4/T_c^{*3}\right]$$

$$= T_c^*/\left(1.26\left[1+(\mu^{*2}/2)^2/3T_c^*\right]\right).$$

Substituting this value in eq. (23b) and using eq. (25), we obtain an expression for the reduced critical density $\rho_c^* = V_c^{*-1}$ for the dipolar fluid

$$\rho_c^* = (1/3.1)+(0.2560/6)(\mu^{*2}/2)^2-0.032745((\mu^{*2}/2)^4+\ldots. \tag{26}$$

Similarly from eq. (23c), the reduced critical pressure P_c^* is expressed as

$$P_c^* = 0.117+(5\times0.09286/6)(\mu^{*2}/2)^2-0.031893(\mu^{*2}/2)^4+\ldots. \tag{27}$$

In eqs. (25)–(27), the first terms are the critical values for the LJ (12-6) fluid when μ*=0. The second and third terms are the second and fourth order perturbation corrections due to the dipole-dipole interactions. The second order correction for T_c^* agrees with the previous result [22]. However, the second order correction for ρ_c^* and P_c^* differs quantitatively from the previous results [22]. The fourth order correction terms in eqs. (25)–(27) are new. From eqs. (25)–(27), it is clear that the values of T_c^*, ρ_c^* and P_c^* increase with increase of μ^{*2} for lower value of μ^{*2}, while they decrease with increase of μ^{*2} for higher values of μ^{*2}. Results of T_c^*, P_c^* and V_c^* based on eq. (22) and eqs. (25)-(27) are compared in Figure 1. They are in good

agreement for lower values of $\mu^{*2}(\mu^{*2} < 1)$. However for higher values of μ^{*2}, they differ. This shows that our theory predicts better results for lower value of μ^{*2}.

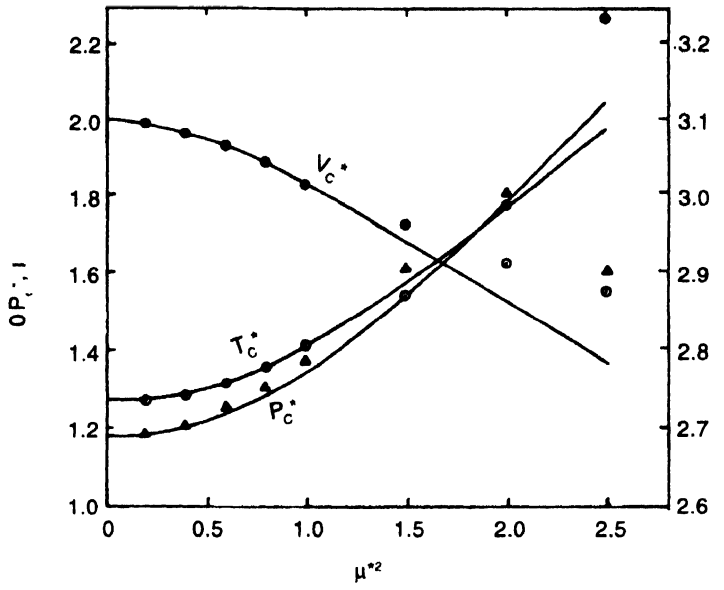

Figure 1. The reduced critical temperature T_c^* Critical volume V_c^* and critical pressure P_c^* of the dipolar LJ (12-6) fluid as a function of μ^{*2}. The points (○ T_c^*, Δ P_c^* and ● V_c^*) represent the series expansion values

Next we calculate the critical temperature T_c, critical volume V_c and critical pressure P_c for molecular fluids such as N_2 and O_2 (with the force parameters given in Table 2) using eq. (22).

The values of T_c, V_c and P_c for N_2 and O_2 are compared with the experimental data [15] in Table 4. The agreement is good.

Table 4. Critical temperature T_c, critical volume V_c and critical pressure P_c for molecular fluids

System		T (k)	V_c (Cm^3)	P_c (atm)	P_cV_c / RT_c
N_2	Theory	129.27	90.22	33.89	0.289
	Expt	126.10	90 10	33 50	0 292
O_2	Theory	154.40	72 58	50 28	0 288
	Expt.	154.40	74.40	49.70	0.292

5. Surface tension

In this section, we apply our theory to calculate the surface tension (ST) along the liquid-gas phase boundary. The ST of the LJ (12-6) fluid is described by [23]

$$\gamma^* \equiv \gamma\sigma^2 / \varepsilon = 2.666(1 - T^*/T_c^*)^{1.27} \tag{28}$$

where $T_c^* = 1.26$. In case of molecular fluid, we replace $\varepsilon \rightarrow \varepsilon_T$ and $\sigma \rightarrow \sigma_T$ in eq. (28). Then the ST of the molecular fluid is expressed as

$$\tilde{\gamma}^* \equiv \tilde{\gamma}\sigma^2 / \varepsilon = (\hat{\varepsilon} / \hat{\sigma}^2)\, 2.666\, (1 - T_T^* / 1.26)^{1.27}, \tag{29}$$

where $T_T^* = kT / \varepsilon_T = T^* / \hat{\varepsilon}$. Eq. (29) is applicable to a molecular fluid over a wide range of temperature. In this approach, the amplitude is modified but the exponent remains a constant with a value of 1.27.

We employ eq. (29) to predict ST γ for N_2 and O_2. These results are reported in Figure 2 as a function of T along with the experimental data [24]. The agreement is good. This shows that the T^* – dependence of $\hat{\sigma}$ and $\hat{\varepsilon}$ is of real physical significance.

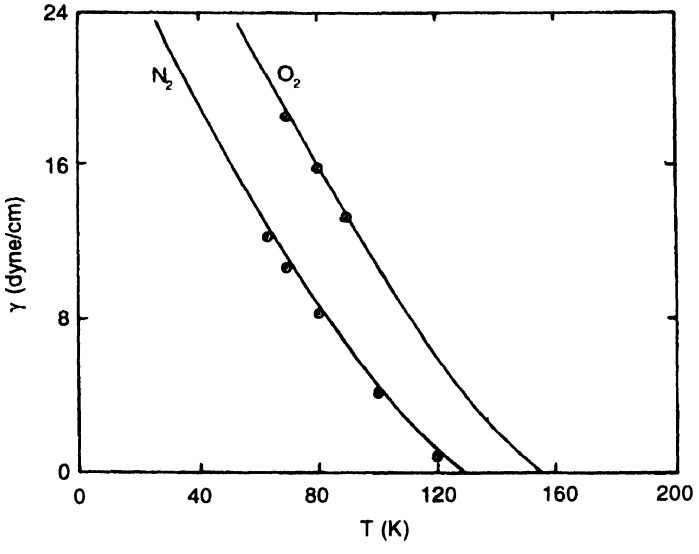

Figure 2. The surface tension γ of N_2 and O_2 as a function of temperature T. The points (Θ) represent the experimental values

6. Liquid-vapour coexistence curve

In this section, we apply our theory to study the behaviour of the liquid-vapour coexistence curve of the molecular fluid. The behaviour of the LJ (12-6) fluid may be described by the following equations [23, 25]

$$V_C^* / V_l^* = 1 + (3/4)(1 - T^* / T_C^*) + (7/4)(1 - T^* / T_C^*)^{1/3} \tag{30}$$

$$V_C^* / V_g^* = 1 + (3/4)(1 - T^* / T_C^*) - (7/4)(1 - T^* / T_C^*)^{1/3}, \tag{31}$$

where V_l^*, V_g^* and V_c^* are the reduced liquid, gas and critical molar volume. Here $T_c^* = 1.26$ and $V_c^* = 3.1$. These equations represent the behaviour of V_C^* / V^* for $T^* / T_C^* \leq 1$.

For molecular fluid, where ε is replaced by ε_T and σ by σ_T, we find [23]

$$V_C^* / V^* \rightarrow (V_C^* / V^*)\, (\sigma^\Lambda / \sigma^\Lambda c)^3,$$

$$T^*/T_C^* \rightarrow T_T^*/1.26,$$

where $\hat{\sigma}_c$ is the value of $\hat{\sigma}$ at $T^* = T^*_c$. Then eqs. (30) and (31) can be expressed as

$$V_C^*/V_l^* = (\hat{\sigma}_C/\hat{\sigma})^3\left[1+(3/4)(1-T_T^*/1.26)+(7/4)(1-T_T^*/1.26)^{1/3}\right], \quad (32)$$

$$V_C^*/V_g^* = (\hat{\sigma}_C/\hat{\sigma})^3\left[1+(3/4)(1-T_T^*/1.26)-(7/4)(1-T_T^*/1.26)^{1/3}\right]. \quad (33)$$

The values of the density ρ, where $\rho^* \equiv v^* - 1$ for N_2 are demonstrated in Figure 3 as a function of $T < T_c$ along with the experimental data [2,26]. The agreement is excellent.

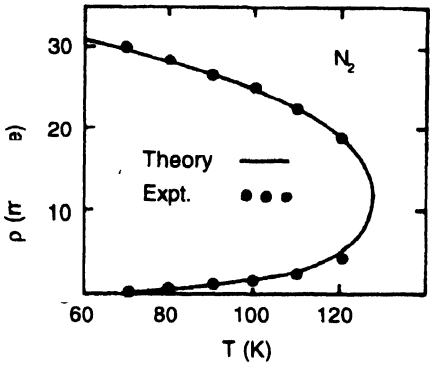

Figure 3. The comparison of theory with experiment for liquid-vapour coexistence curve of N_2.

7. Transport properties of molecular fluids

Lastly, we apply out theory to estimate the transport properties (TP's) such as shear viscosity μ and thermal conductivity λ of molecular fluids. We assume that the structure of a dense fluid is similar to that of a hard sphere (HS) fluid of properly chosen hard sphere diameter d_T. The TP's of the ELJ (12-6) fluid may be evaluated through the evaluation of the TP's of the HS fluid.

7.1 Effective diameters:

To obtain the effective diameter of the fluid, we divide the effective pair potential $\psi(r)$ into a reference part ψ_0 and perturbation part ψ_p, according to theWeeks-Chandler-Andersen (WCA) scheme [17]

$$\psi(r) = \psi_0(r) + \psi_p(r), \quad (34)$$

where

$$\psi_0(r) = \psi(r) + \varepsilon_T, \quad r < r_m;$$
$$= 0, \quad r < r_m; \quad (35a)$$

and

$$\psi_p(r) = -\varepsilon_T, \quad r < r_m;$$
$$= \psi(r), \quad r < r_m, \quad (35b)$$

where $r_m = 2^{1/6}\,\sigma_T$ for the ELJ (12-6) potential. Using this perturbation scheme, the free energy A for the molecular fluid is given by

$$A = A_0 + (1/2)\,N\rho \int g_0(r)\,\psi_p(r)dr\,, \tag{36}$$

where A_0 and g_0 are, respectively, the free energy and radial distribution function (RDF) of the reference fluid.

A_0 of the reference system can be obtained by a blip function expansion [17] about HS system interacting through $u_{HS}(r)$,

$$\begin{aligned} u_{HS}(r) &= \infty\,, \qquad r < d_T\,; \\ &= 0, \qquad r < d_T \end{aligned} \tag{37}$$

where d_T is the effective hard sphere diameter, which is determined by the Verlet-Weis method [16] and given by

$$d_T = d_B\left[1 + (\sigma_{11}/2\,\sigma_{00})\,\delta\right], \tag{38a}$$

where

$$\begin{aligned} d_B &= \int (1 - \exp(-\beta\,\psi_0(r)))\,dr\,, \\ \delta &= \int ((r/d_B) - 1)^2\,(d/dr)\,(\exp[-\beta\,\psi_0(r)))\,dr\,, \\ \sigma_{00} &= (1 - \eta/2)\,(1-\eta)^{-3} \\ \sigma_{11} &= (1 - 7.5\eta + 0.5\eta^2 - 5.7855\eta^3 - 1.51\eta^4)\,(1-\eta)^{-4} \end{aligned} \tag{38b}$$

Here $\eta = \pi\,\rho\,d_T^3/6$ is the packing fraction.

7.2 Transport properties :

The TP's of the LJ (12-6) fluid can be estimated through the evaluation of the TP's of the HS fluid with the properly chosen effective diameter. This approach can be extended to evaluate the TP's of the ELJ (12-6) system. We employ the revised Enskog theory (RET) of Beijeren and Ernst [27] to estimate μ and λ of the HS fluid. They are given by

$$\mu = [g_{HS}(d_T)]^{-1}\,[1 + (4/5)\,L + 0.7615\,L^2]\,\mu_0\,, \tag{39}$$

$$\lambda = [g_{HS}(d_T)]^{-1}\,[1 + (6/5)\,L + 0.7575\,L^2]\,\lambda_0\,, \tag{40}$$

where

$$\mu_0 = (5/16\,\pi\,d_T^{\,2})\,(\pi mkT)^{1/2}\,, \tag{41}$$

$$\lambda_0 = (75k/64\,\pi\,d_T^{\,2})\,(\pi\,kT/m)^{1/2}\,, \tag{42}$$

$$L = 4\,\eta\,g_{HS}(d_T)\,. \tag{43}$$

Here, m is mass of a particle and $g_{HS}(d_T)$ is the Equilibrium radial distribution function (RDF) of the HS fluid at the contact.

The effective hard sphere diameter d_T and RDF $g_{HS}(d)$ may be determined from the experimental values of the second virial coefficient B(T) and equation of state PV/NkT, respectively [28]. However, in the present case, the diameter d_T is determined using eq. (38), and the equilibrium RDF $g_{HS}(d_T)$ is given by [29]

$$g_{HS}(d_T) = (1 - \eta/2)(1 - \eta)^{-3} \tag{44}$$

8. Results and discussion

We calculate the TP's of fluid N_2 using ELJ (12-6) and LJ(12-6) models with parameters given in Table 2. We present the shear viscosity μ of fluid N_2 in Figure 4 at T = 250°K. Experimental data [16] and result obtained previously by Sinha [11] with GOCE model are also reported. The agreement is good particularly at low density. This result is a bit better than the result of the GOCE model given by Sinha. From the figure it is clear that the angle-dependent interaction enhance the value of μ.

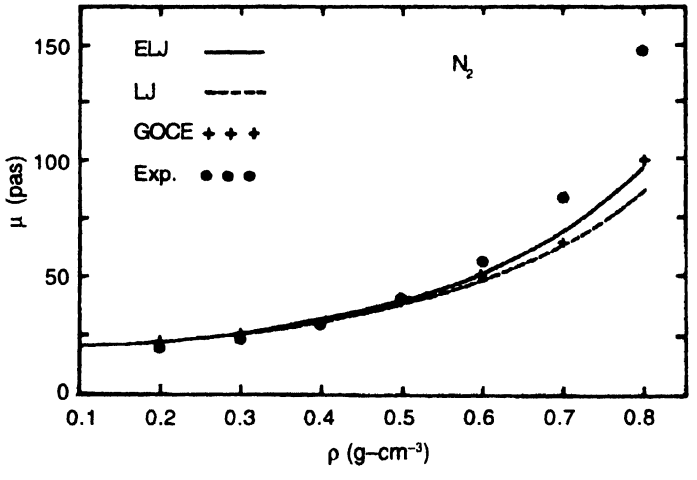

Figure 4. The shear viscosity μ of N_2 as a function of ρ at T = 250°K

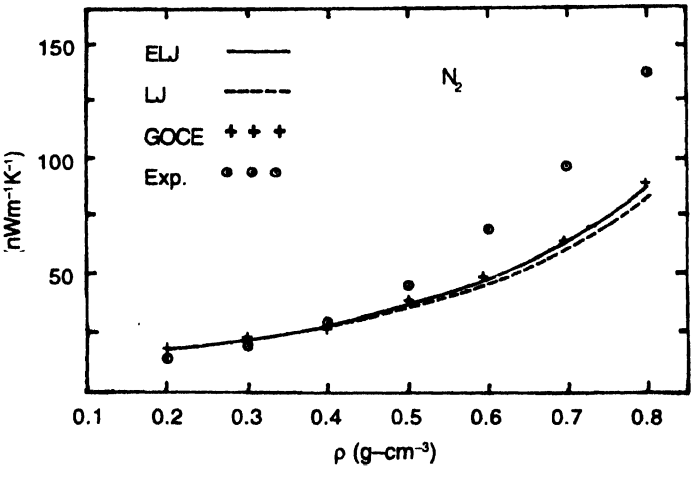

Figure 5. The thermal conductivity λ of N_2 as a function of ρ at T = 130°K.

Figure 5 demonstrates our results for thermal conductivity λ of fluid N_2 at T = 130°K. The results obtained by Sinha [11] and the experimental data [16] are also shown there. The agreement is good except at high density. The angle dependent interaction enhances the value of λ also.

9. Concluding remarks

The effective pair potential is expressed in the LJ(12-6) form by simply replacing $\sigma \rightarrow \sigma_T(T^*)$ and $\varepsilon \rightarrow \varepsilon_T(T^*)$. Then the system can be treated as the LJ(12-6) system. The ELJ (12-6) potential is employed to estimate the thermodynamic and transport properties of molecular fluids over a wide range of temperature and density. In all these cases, the agreement with experimental data (where available) is good.

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Appendix A

In this Appendix, expressions for the coefficients A_m appearing in the right hand side of eq. (8) are given as

$$A_6 = 1+(1/2)(\alpha^* \mu^{*2})+(1/12\,T^*)(\mu^{*2})^2\,, \tag{A.1}$$

$$A_8 = (3/4)\,\alpha^* Q^{*2}+(1/4\,T^*)(\mu^{*2} Q^{*2})\,, \tag{A.2}$$

$$A_{10} = (7/20\,T^*)(Q^{*2})^2\,, \tag{A.3}$$

$$A_{12} = 1-(4/5T^*)\,K^2\,(1+1.9\,K^2)+(7/1800\,T^{*3})(\mu^{*2})^4 \tag{A.4}$$

$$A_{11} = (1/5T^*)\,Q^{*2}\,[\,(36/5)\,K^2+(1/T^*)(\mu^{*2})^2] \tag{A.5}$$

$$A_{13} = (6/35T^{*2})\,\mu^{*2}\,(Q^{*2})^2\,, \tag{A.6}$$

$$A_{15} = (18/245T^{*2})\,(Q^{*2})^3\,. \tag{A.7}$$